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ULTRAVIOLET-OZONE AND ULTRAVIOLET-OXIDANT TREATMENT OF PINK WATER

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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Pink water, a solution of trinitrotoluene (TNT and other nitrobodies) is a major pollutant at AAP's which manufacture TNT and load, assemble and pack bombs and other ammunition. Two of the new technologies being investigated as alternatives to carbon adsorption, which is currently used to purify pink water, are covered in this report. One method involves the use of ultraviolet (uv) ozone; the other, uv-oxidant.

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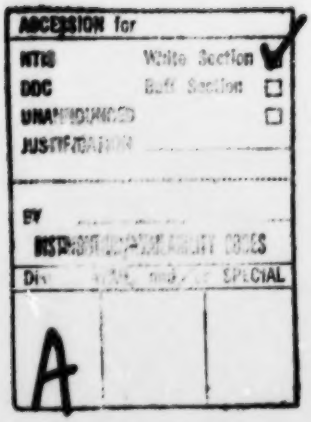
In the uv-ozone study, a pilot system with a volume of 3.79 cubic meters per day was evaluated. This system reduced dissolved TNT and RDX to less than one milligram per liter with no by-products requiring disposal. A larger, 18.9 cubic meter per day plant, is proposed.

In evaluating the uv-oxidant process, commercially available uv-light, water-purification units were used in conjunction with oxidants such as hydrogen peroxide or oxone, a blend of potassium persulfate oxidants. Variables such as film depth, dilutions, uv wavelength, and operation of the units in series rather than in parallel, were examined in optimizing the system.

FOREWORD

Experimental work for the uv-ozone portion of this study was conducted by Westgate Research Corporation, West Los Angeles, California. The uv-oxidant study was conducted by the Naval Weapons Support Center at Crane, Indiana.

This project was conducted in conjunction with the US Environmental Protection Agency, under Interagency Agreement D6-0059. Dr. Herbert S. Skovronek of the Industrial Waste Treatment Research Laboratory, Edison, NJ, served as the EPA's Project Officer.



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INTRODUCTION

Pink water is generated by (1) trinitrotoluene (TNT) manufacturing plants, (2) load, assemble, and pack (LAP) operations, and (3) unloading or demilitarizing TNT-loaded munitions. Pink water from manufacturing operations may contain α TNT, TNT isomers, and dinitrotoluenes (DNT), while pink water generated by LAP and demilitarization operations may contain α TNT, cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), and wax.

The volume and concentration of pink water streams vary widely, but, at full mobilization, volumes of 378.5 m^3pd (100,000 gpd) per line at concentrations of 100 to 150 ppm are typical (ref 1). Currently, activated carbon is the most widely used process for pink water abatement. The carbon is used once, then burned, which results in a high cost operation and an air pollution problem. Systems for thermal regeneration and carbon reuse tried in the past involved a high risk of explosion and a high loss of carbon. A new thermal regeneration process using rotary kilns has been piloted and appears to be safe and cost effective, but has yet to be implemented. Consequently, new technologies for abatement of pink water, such as the uv-ozone and uv-oxidant processes described in this report, continue to be investigated.

The uv-ozone studies helped establish approximate operating levels for the number of uv lamps per stage and ozone mass flow required to treat actual pink water. The uv-oxidant studies established the film depth and oxidant concentration required.

UV-OZONE TREATMENT OF PINK WATER

The objective of the uv-ozone testing was to establish design criteria and cost figures for a 378.5 m^3pd (100,000 gpd) pink water treatment plant. Test runs were made in a 1000 gpd uv-ozone reactor. Operating and design variables for the minimum power demand and retention time required to obtain an effluent containing less than 1 mg/L of TNT and less than 1 mg/L of RDX were defined.

Description Of Ultrox Pilot Plant

The Ultrox[1] pilot plant, recently developed by the Westgate Research Corporation, is designed to demonstrate the practicality and cost effectiveness of uv-ozone oxidation for destroying organics in wastewater. The pilot plant can vary (1) UV light input and intensity, (2) ozone introduction rate, (3) mixing, and (4) water flow. The reactor is made of 304 stainless steel, passivated and electropolished to reduce chemical attack and increase reflectivity. A separate NEMA cabinet houses the ballasts from the UV lamps.

The reactor can accommodate up to 30 low-pressure, 65-watt uv lamps and has six operating stages. From 0 to 30 lamps can be turned on in a test run. Ozone is uniformly diffused from the base of the reactor through spherical, porous spargers, a procedure that generates gas bubbles of less than 2.5 mm diameter to obtain maximum mass transfer. The number of spargers can be varied from stage to stage, and the overall pattern of ozone introduction and diffusion can be changed as desired.

The reactor is designed for low-pressure operation (2 psig maximum) to reduce the cost for pumping water and compressing air for ozone generation. Low-pressure operation not only provides greater safety but also reduces the thickness, weight, and cost of construction materials.

Pilot Plant Operation

The flow rate of the incoming pink water is measured by a rotameter located between the pump and the reactor inlet. The water is fed to the reactor by the use of a sealless, magnetic, gear-type drive pump with integral,

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1. Registered trademark

solid-state speed control. The drive pump varies the flow of pink water through the reactor from 7.6×10^{-4} m^3/min to 7.6×10^{-3} m^3/min (0.2 to 2.0 gpm), and the retention time will vary from 37 to 375 minutes. In each stage the water is contacted by the ozone and, in certain stages, by UV light.

The purified water, as it leaves the reactor, overflows into a gas-water separator to eliminate any entrainment of water in the exhaust gas and then drains by gravity to a receiving sump. No internal level controls are required within the reactor.

Test Procedures

Previous experience with pink water and waters of similar composition proved that the following variables have the greatest influence on total power demand and reactor size:

1. Ozone concentration in sparging gas.
2. UV light intensity.
3. Placement of uv lamps within reactor.
4. Temperature, composition, and concentration of incoming water.
5. Flow rate.

Preliminary Testing

The TOC of the ARRADCOM pink water sample was 68 mg/L, which was derived from 140 mg/L TNT, 22 mg/L RDX, and 10 mg/L wax. The synthetic solution for the shakedown tests was mixed to contain this concentration of TNT; however, large amounts of undissolved TNT were present which reacted as the oxidation progressed so that it was difficult to control operating conditions and effluent quality. This problem was corrected by dissolving small quantities of TNT in boiling water, diluting it, and inserting an in-line filter at the inlet of the pilot plant to remove residual suspended solids. Several experiments were carried out under these conditions (Table 1). These experiments helped to establish approximate operating levels for the number of UV lamps per stage and ozone mass flow required to treat

Table 1. UV-Ozone treatment of TNT in water

Test No.	Temperature (°C)	Total organic carbon (mg/L)[a] Influent	Stages 1-3[b] (118 min. residence)	Stages 4-6[c]
1022	36	60	13	3.0
1023	32	55	7	2.5
1024	26	66	5	1.2
1025	33	66	5	2.0
1026	33	54	10	6.5

a. Based on a flow rate of 1200 ± 100 mg of ozone per minute.

b. 7 ± 2 W uv per mg TOC

c. 40 ± 20 W uv per mg TOC

actual pink water.

With this high concentration of TNT, additional ozone generator capacity was needed. Both an OREC[2] O3B2-0 and a Welsbach[2] W-20 were used to provide up to 2 g/min ozone (in oxygen), or approximately 1.8-2.0% ozone in oxygen.

Pink Water Tests

Results of pilot plant tests using ARRADCOM pink water are summarized in table 2. The first test (No. 1027) was run under the same approximate conditions as Test No. 1026 for a synthetic sample (TNT in water). Greater resistance to oxidation occurred with the pink water than with the synthetic solution and the TOC was only reduced to 17 mg/L during a 240-min. residence time. The residence time and number of uv lamps had to be increased in subsequent tests (1028 and 1029) to obtain a greater degree of oxidation. It appears that the reduced reactivity in the pink water sample was caused by the presence of wax and RDX which were not present in the synthetic sample.

A comparison of pink water and the synthetic sample based on the results of tests No. 1024 and 1029 is shown in table 3. The ozone-to-organic carbon ratios are about the same for the first three stages and the last three stages; however, the uv input power-to-carbon ratio had to be increased in both the first three stages and second three stages to achieve 3 mg/L TOC and 5 mg/L TOC in the pink water after six stages.

Specific Analysis

Less than 1 mg/L TNT and 1 mg/L RDX remained in the effluent, but there was also some unidentified solid residue in both the pink water and the synthetic sample (table 4). Test No. 1029 indicated that the TNT and RDX levels were below 1 mg/L after the pink water had passed through the first three stages of the reactor. This result was most encouraging, since at these operating conditions the residence time, the number of UV lamps, and the ozone mass flow input can be reduced by half of the total values used in test No. 1029.

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Table 2. UV-Ozone treatment of ARRADCOM pink water

Test No.	Temperature (°C)	Total Organic Carbon (mg/L)		
		Influent	Stages 1-3[c]	Stages 4-6[d]
1027[a]	29	68	22.0	17.0
1028[b]	30	67	6.5	5.0
1029[b]	30	70	5.0	3.0

a. Residence time - 118 min.

b. Residence time - 177 min.

c. 1200 ± 100 mg ozone per min; 7 ± 2 W uv per mg TOC

d. 1200 ± 100 mg ozone per min; 40 ± 20 W uv per mg TOC

Table 3. Comparison of synthetic sample and ARRADCOM pink water tests

Test No.	Ozone/TOC mass ratio (mg/mg)		Input, W/mg		TOC (mg/L)		
	Stages 1-3	stages 4-6	stages 1-3	stages 4-6	Influent	stage 3	stage 6
1024[a]	15	198	7	60	66	5	1.2
1029[b]	13	180	11	140	70	5	3

a. Synthetic sample

b. Pink water

Table 4. Analysis of synthetic sample and ARRADCOM pink water

Test No.	Sample	TNT (mg/L)	RDX (mg/L)	Solid Residue (mg/L)
1020-1	Synthetic feed	76	-	-
1020-2	Synthetic effluent	<1	-	-
1023-2	Synthetic effluent	<1	-	11
1024-2	Synthetic effluent	<1	-	8
1025-2	Synthetic effluent	<1	-	6
1028-2	Pink water effluent	<1	< 1	12
1029-1	Pink water effluent after stage 3	<1	< 1	9
1029-2	Pink water effluent after stage 6	<1	< 1	11

Discussion of Test Results

The mass ratio of ozone to TOC in Test No. 1029 for the first three stages was 13, which is 1.6 times the stoichiometric ratio for carbon oxidation to CO_2. Bench and pilot plant tests on a variety of wastewaters indicated that the minimum stoichiometric ratio of ozone to TOC usually is between 1.3 and 2.0, depending on the original TOC concentration and the chemical structure of the organic contaminants. (However, this calculation does not include hydrogen and nitrogen oxidation in either case.) On that basis, the pink water appears to be reacting normally.

It is more accurate to represent the total oxidation of TNT and RDX as follows:

TNT

$$C_6H_2CH_3(NO_2)_3 + 18\ O_3 \longrightarrow 7\ CO_2 + 3\ HNO_3 + 18\ O_2 + H_2O$$

RDX

$$C_3H_6N_3(NO_2)_3 + 18\ O_3 \longrightarrow 3\ CO_2 + 6\ HNO_3 + 18\ O_2$$

The pink water contained 140 mg/L TNT and 72 mg/L RDX. According to the above equations, the theoretical amount of ozone required per liter to carry out complete oxidation is 813 mg. Since the testing found that 910 mg/L was required to obtain an acceptable effluent, the ratio of actual to stoichiometric ozone is 1.12:1 (or an ozone efficiency of 89.3%). Of course, part of the ozone may be lost by autodecomposition or volatilization.

Although a greater number of UV lamps was required to oxidize the pink water than the synthetic TNT in water solution, the number of lamps required per square meter and reaction stage has not been defined. Further tests are required to establish these exact numbers.

Design of UV-Ozone Pilot Plant

With data obtained from the 3.79 m^3pd (1000 gpd) the following design criteria were established for the 18.9 m^3pd (5000 gpd) pilot plant:

Dimensions

Reactor wet volume.....2.6 m^3 (675 gal)

Reactor dimensions (W x L x H).0.9 x 1.8 x 1.5 m

(0.3 x 6 x 5 ft)

Water flow rate .....18.9 m^3pd (5,000 gpd)

No. of UV lamps @ 65 W/lamp....144

Ozone required.....17 kg/day (37.5 lb/day)

Assembly

The major components of the pilot plant are the reactor assembly, the NEMA ballast enclosure, and the ozone generator. The reactor assembly and the NEMA ballast enclosure are assembled on the same skid and the ozone generator is mounted on a separate skid.

The reactor assembly (fig 1) consists of a stainless steel tank with baffles and a cover assembly made up of the reactor cover, ozone diffuser, UV lamps, and supporting structure.

Construction

The reactor tank, 0.91m x 1.83m x 1.52m (3 ft x 6 ft x 5 ft) deep, is fabricated from 0.48cm (3/16 in.) 316 stainless steel sheet. The bottom of the tank is formed from stainless steel. All parts are certified heliarc welded. A 10.2cm (4 in.) wide lip is welded to the top of the tank to form a gasket flange. A groove is cut into the flange to accommodate a rectangular Hypalon[3] seal to enclose the reactor. The tank is mounted by bolting onto the metal skid.

Five baffles are located longitudinally to create six reaction stages. Water flows in an undulation path from stage to stage (fig 2). The baffles are designed for easy removal so that the number of reaction stages can be altered, as desired.

The ozone inlet manifolds, lamp venting tubes, and lamp

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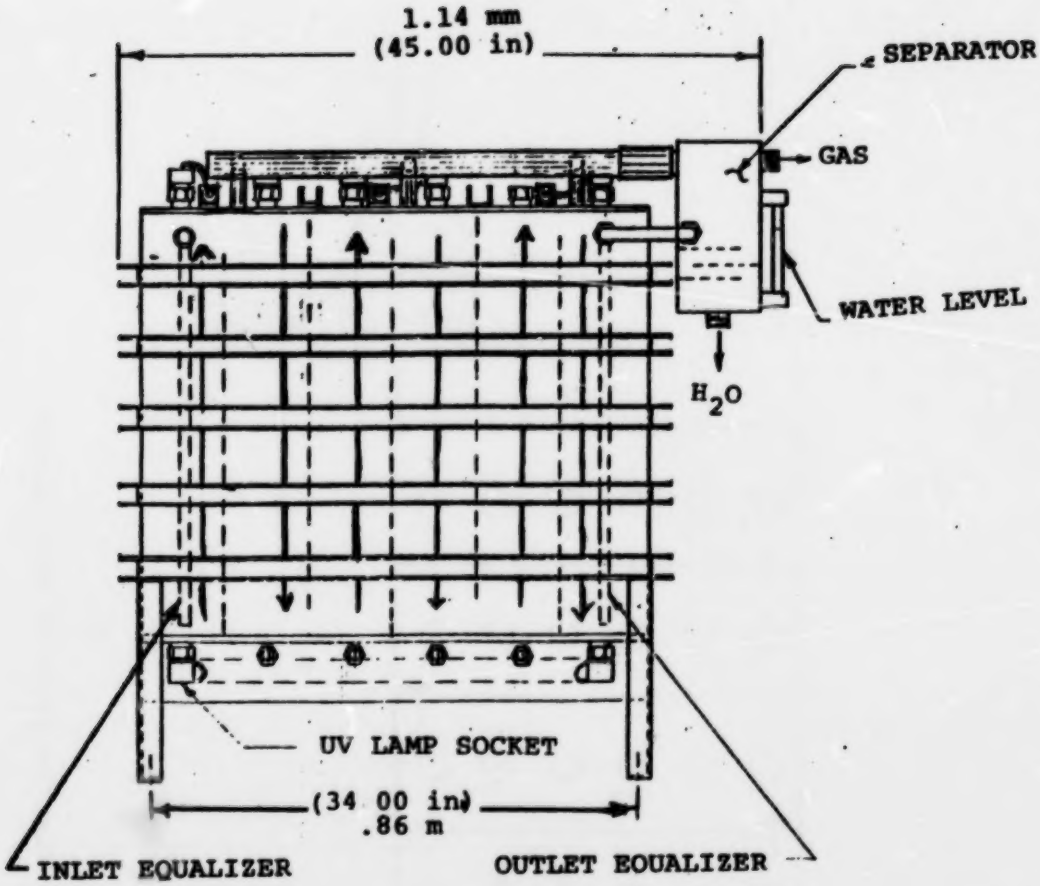

Fig 1 UV-ozone reactor assembly

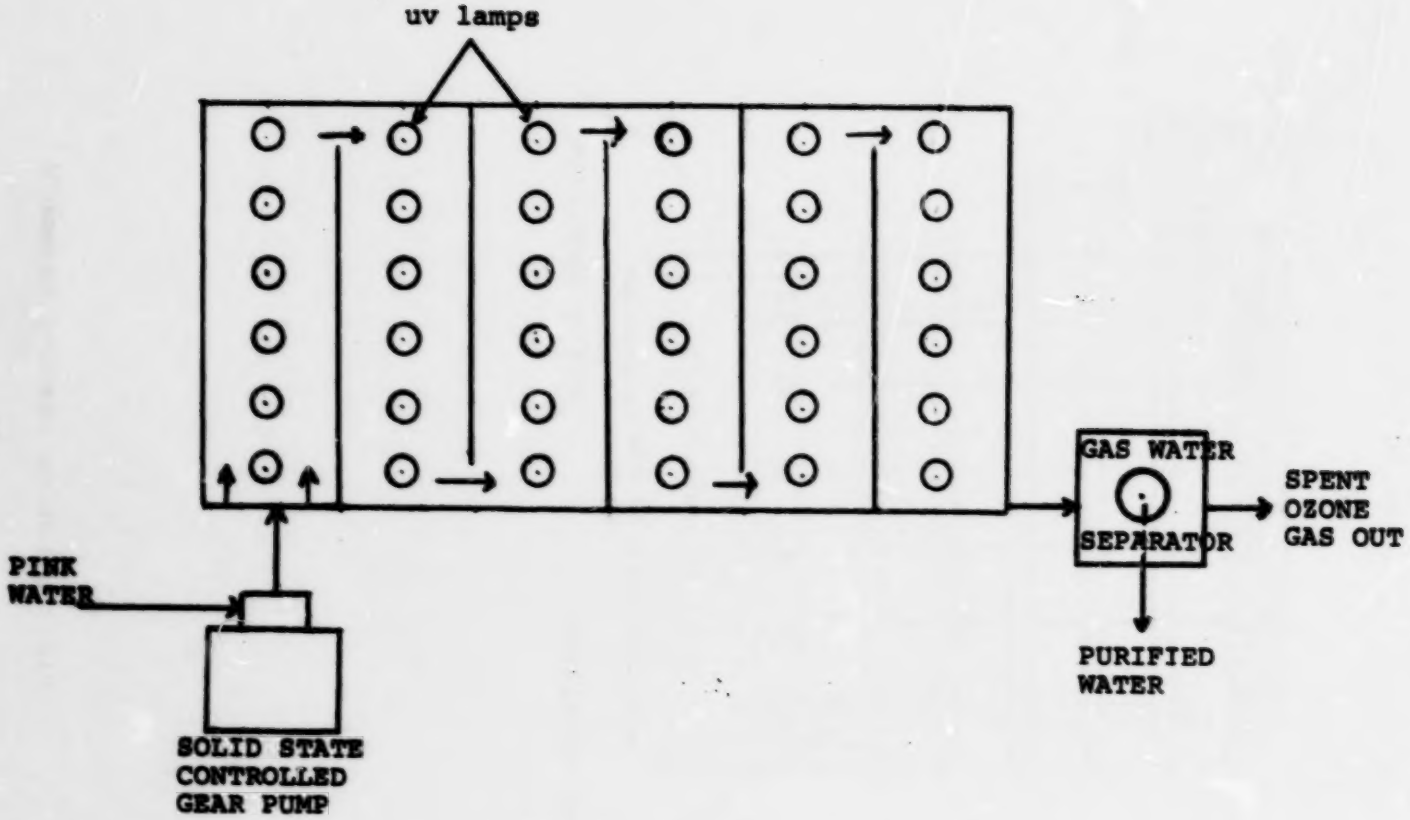

Figure 2. Pattern of water flow through pilot plant reactor

conduits are welded across the reactor and provide adequate crosswise stiffening. Longitudinal stiffening is achieved by three strips of stainless steel welded to the cover plate, the manifolds, the ozone air vent, and the wiring conduits. A diagram of the proposed pilot system is shown in figure 3.

Cover Assembly

The following openings are punched into the cover plate:

1. One hundred and forty four holes, 2.86 cm (1 1/8 in.) in diameter (in a geometric pattern) for the quartz tubes that enclose the UV lamps. Nipples are welded at the top surfaces of these openings so that the quartz tubes are sealed to the cover by compression nuts with O-rings.

2. Six holes, 2.54 cm (1 in.) diameter, for the spent ozone gas outlets.

3. Six holes, 3.81 cm (1 in.) square, for mating with the lamp support structure.

4. Six holes, 1.59 cm (5/8 in.) diameter, for the outboard lamp support and cooling air vent lines.

5. Two nipples, 3.81 cm (1½ in.) NPT, for water inlets.

The lower lamp support structure consists of 3.81 cm (1½ in.) square tubes with a 0.159 cm (0.0625 in.) wall thickness. Holes of 2.54 cm (1 in.) diameter are drilled on the upper side of the tubes at appropriate positions to install the quartz tube support and sealing assemblies which are welded to the upper side of the tube. A 1.27 cm (½ in.) diameter hole is drilled through the outboard end of the conduit to attach the vent tube which also acts as a support for the end of the square tube. The center of the square tube is supported by welding the ozone line to the diffusers running parallel to the conduits.

NEMA Ballast Enclosure

A standard 1.52 cm x 0.91 m x 0.31 m (5ft x 3ft x

UV OZONE REACTOR:

18.9 m^3pd (5,000 gpd)

OZONE GENERATOR:

(Welsbach Specification)

37.5 lb per day 1% concentration

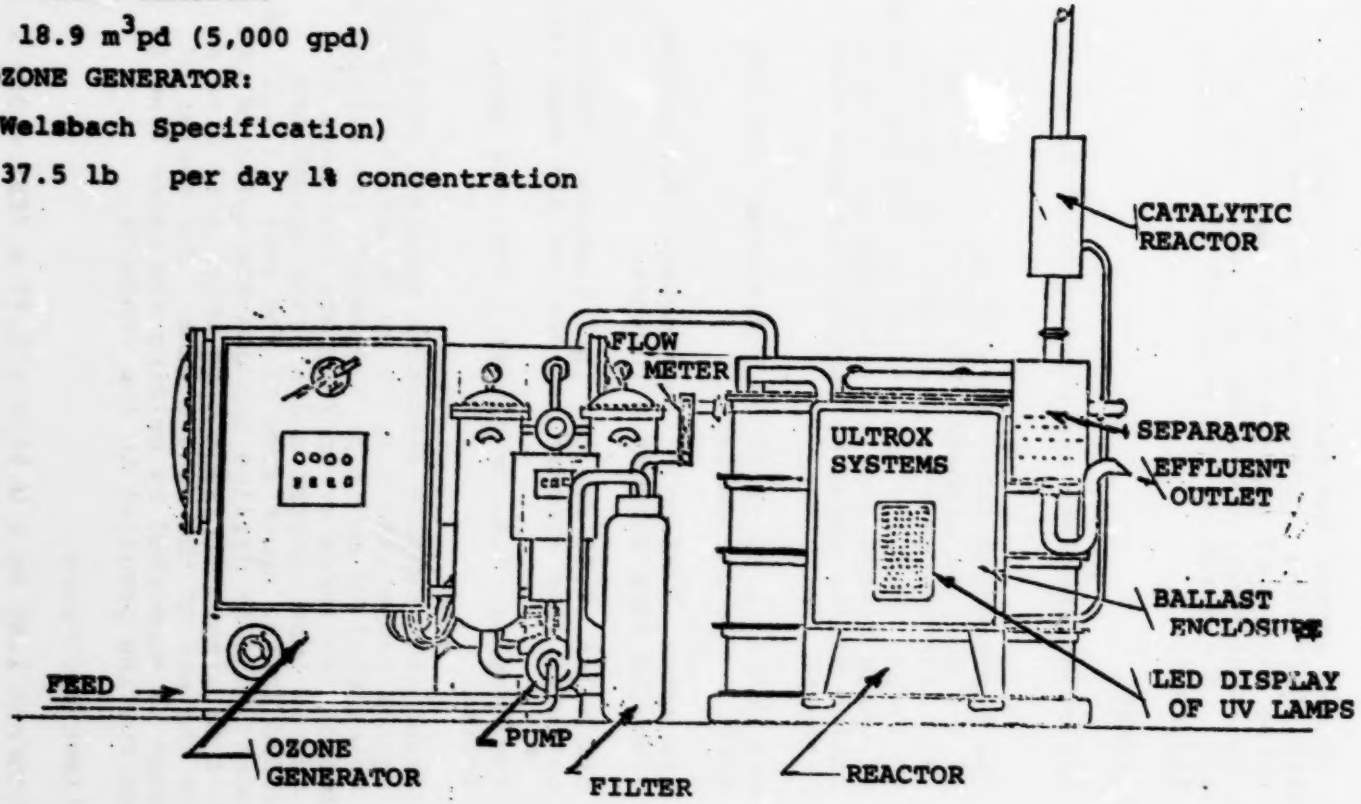

Fig 3. The 920 m^3pd (5000 gpd) pilot plant assembly

1ft) deep, 16-gauge NEMA cabinet is used to contain and cool 72 lamp ballasts. The ballasts are mounted on racks in six rows within the cabinet. A rotary air blower, mounted at the base of the cabinet, directs the air upward for cooling the ballasts. The air exits at the top of the cabinet.

The cabinet door contains a mounted LED display behind a glass window. The display shows visually the number UV lamps "on" in the reactor. Elastomer gasketing and springloaded screw clamps seal the door.

Ozone Generators

A number of manufacturers can supply generators which meet the 18.9 m^3/d (5,000 gpd) pilot plant criteria of 17 kg (37.5 lb) of ozone per day. From some manufacturers, such as OREC or PCI, two 9.1 kg (20 lb) per day ozone generators would be required since neither one has an off-the-shelf 18.2 kg (40 lb) generator. The Welsbach generator is oversized, but it can produce 18.2 kg (40 lb) efficiently by lowering the input voltage by means of a variable voltage transformer.

UV-OXIDANT TREATMENT OF PINK WATER

Bench-scale studies researching the effects of short wavelength UV-light and H_2O_2 in the treatment of explosive-contaminated effluents have shown this treatment to be very successful (ref 2). This photo-oxidative treatment appears to be effective not only in decolorizing pink water, but also in destroying TNT, RDX, HMX, and other nitrobodies with a concurrent reduction in TOC concentration. These effects have been determined by gas, liquid, and thin-layer chromatography (GC, LC, TLC), total organic carbon (TOC), and 14C-labeled TNT assays.

The economic feasibility of using commercially available UV water purification units in conjunction with an oxidizing agent was investigated during the bench-scale studies. Variables, such as oxidants, film depth, serial passaging, and wavelength of UV light, were also examined for optimization of treatment parameters.

Description of UV-Oxidant Pilot Plant

A small-scale pilot system was designed incorporating four UV-light,water purification units connected in series. These were Model 2000 units manufactured by the Ultradynamics Corporation of Santa Monica, California, with four 40-W mercury vapor lamps (254 nm) protected by quartz jackets that are continuously cleaned by a hydraulically operated wiper assembly. The liquid capacity of each chamber is approximately 22.8 L (6 gal). The maximum film depth of approximately 5.72 cm (2¼ in).

Pink water obtained from a bomb loading and steam-out operation at the Naval Weapon Support Center, Crane, IN, was used in the study. Before being pumped into the system, the water was filtered to remove suspended solids which could interfere with the treatment. Because its intense color would negatively affect the efficiency of the system, the pink water was diluted 1:1 or 1:3 with tap water to yield the following average explosive and TOC concentrations (mg/L):

	1:1 dilution	1:3 dilution
TNT	70.9	34.1
RDX	72.4	27.0

(cont)	1:1 dilution	1:3 dilution
HMX	9.4	4.1
TOC	52.6	27.0

Previous studies (ref 2) determined that 0.1% (H_2O_2) is the optimum concentration to use in treating pink water. A 35% solution of H_2O_2 (Fisher Chemical Co.) was added to the pink water to yield a final concentration of 0.1% H_2O_2. The water was recycled from a reservoir through the UV units at a flow rate of 2.73 m^3/hr (720 gph) in a continuous flow mode. Only 7.58 to 11.4 L (2 to 3 gal) of the 128.9 L (34 gal) solution were retained by the fast reservoir. Tubing volume is considered negligible because of the fast flow rate. The actual residence time of the liquid in any one unit is about 0.008 hr. A smaller commercial unit has been used to study the efficiency of the photo-oxidative treatment of pink water with respect to film depth. A Model 500 unit (also manufactured by Ultradynamics Corp.) with a 2.54 cm (1 in) film depth was used. The static capacity of its chamber is approximately 2.84 L (3/4 gal). It resembles the UV 2000 unit in structure and appearance, One gallon of pink water (undiluted or diluted) containing 0.1% H_2O_2 was recirculated through the unit and back into a reservoir at a flow rate of approximating 0.4 m^3/h (105 gph).

Parameter Variations for Optimization of the System

Oxidizing Agents and Film Depth Studies

To test the effectiveness of incorporating a different oxidizing agent, a monopersulfate compound, Oxone[4] was substituted for the H_2O_2 in a number of studies using the UV-2000 and UV-500 system. In both systems, overall efficiency was significantly increased by using 0.3% Oxone in place of 0.1% H_2O_2. Table 5 illustrates the results of treatment of a 1:3 diluted pink water solution in the UV-2000 (4-unit system) at a flow rate of 2.73 m^3/d (720 gpd),

4. Oxone is a mixture of potassium monopersulfate, potassium hydrogen sulfate, and potassium sulfate, manufactured by E.I. duPont de Nemours, Inc.

Table 5. Oxidation in the UV-2000 and UV-500 systems with Oxone or H_2O_2

System/Oxidant%	UV Exposure (hr)	Water analyses (mg/L) TNT	RDX	HMX	TNB[a]	TOC	PNA[b]
UV-2000	0.0	30.0	26.8	3.0	0	24.8	TNT + 2
0.1 H_2O_2	3.0[c]	0.01	0.01	0.02	2.53	5.6	TNB + 3
	5.0	0.01	0.01	0.02	2.8	1.6	TNT + 3
UV-2000	0.0	34.0	27.4	2.8	0	24.2	TNT + 2
0.3 oxone	3.0[c]	0.01	0.01	0.0	0	0.1	0
	5.0	0.01	0.01	0.02	0	0.2	0
UV-500	0.0	29.0	20.6	3.1	0	23.0	TNT + 2
0.1 H_2O_2	0.5	0.8	0.01	0.02	0.9	17.4	TNT, TNB + 4
	1.5[c]	0.05	0.01	0.02	2.8	8.0	TNB
UV-500	0.0	29.0	20.6	3.1	0	23.0	TNT + 2
0.3 oxone	0.5[c]	0.3	0.01	0.02	1.5	7.6	TNT, TNB + 2
	1.5	0.01	0.01	0.02	0.06	1.8	0

a. Trinitrobenzene

b. Polynitroaromatic compounds as detected by TLC. All compounds present at barely detectable levels in most cases. Except for TNB, the other polynitroaromatics remain to be identified.

c. Hour decolorization noted (app).

and in the UV-500 system at a flow rate of 0.4 m^3/h (105 gph) using either 0.1% H_2O_2 or 0.3% Oxone. The solutions were analyzed by liquid, gas, and thin-layer chromatography for explosive residues and TOC concentrations.

From the results in table 5 it is evident that Oxone is far superior to H_2O_2 with respect to decolorization time, TNT elimination, and degradation of polynitroaromatic by-products with corresponding reductions in TOC concentrations. These results also show that the 2.54 cm (1 in) film depth of the UV-500 system (compared to the 5.72 cm (2½ in) film depth of the UV-2000 system) enhances the efficiency of the treatment with either oxidizer.

Various concentrations of oxone were also studied, and the potential of a combination H_2O_2/ Oxone treatment was examined. Because of the limited time available, only the effects of 0.3% and 0.2% Oxone on diluted pink water in the UV-2000 units, and 0.3% and 0.7% Oxone on undiluted pink water in the UV-500 system were examined. A combination of 0.1% H_2O_2 and 0.1% Oxone was also examined in the UV-2000 system. Table 6 illustrates the parameters and results of the treatment.

Treatment of 1:3 diluted pink water in the UV-2000 system with 0.3%, 0.2% and 0.1% Oxone and 0.1% H_2O_2 are comparable. The TOC levels were appreciably reduced and no detectable amounts of explosives or polynitroaromatics were found after 3 hours of exposure. Treatment of an undiluted pink water solution with 0.7% Oxone in the UV-500 system is not as efficient as treatment of a 1:3 diluted pink water solution with 0.3% Oxone, but it is feasible if environmental trade-offs are allowed. The same is true of a 1:1 dilution of pink water treated in the UV-2000 system with 0.3% Oxone.

Flow Rates and Operations of Units In Series

Two flow rates were examined in the UV-2000 system. There appeared to be no major difference in results between flow rates of 2.04 and 2.73 m^3ph (540 and 720 gph) while operating in a continuous flow mode. If the ultimate treatment were direct passage and not recirculation of the pink water through the UV system, the flow rate would not be critical, but the total UV exposure time or contact time of the solution in the units would be. Operation in a continuous flow mode through one to four UV-

Table 6. Analyses of various concentrations of Oxone and Oxone and H_2O_2

Operating parameters			Original/Final Analytical results (mg/L)					
Dilutions	Oxidizing agent (%)	UV contact time (hr)	TNT	RDX	HMX	TNB	TOG	TLC
1:4	0.3 Oxone	3	28/0.01	26/0.01	27/0.02	trace/ 0	22.8/0.3	TNT/0 +2PA
1:2	0.3 Oxone	3	64/0.01	55/0.1	8.5/0.02	trace/ 0.4	46.1/3.4	TNT/TNB +2PA
1:4	0.2 Oxone	3	23/0.01	19/0.01	2.4/0.02	trace/ 0	21.8/0.4	TNT/0 +2PA
1:4	0.1 Oxone 0.1 H_2O_2	3	23/0.01	20/0.01	2.5/0.02	trace/ 0.1	25.0/0.9	TNT/0 +2PA
			UV-5000 system					
0	0.7 Oxone	6	138/0.02	3.1/0.02	0.02/15.0	0/1.1	86.6/8.95	TNT/TNB +3PA/+1PA
1:4	0.3% Oxone	3	29.0/0.01	20.6/0.01	3.1/0.02	0/0.3	23.0/1.8	TNT/0 +2PA

2000 units in series appeared to have no major effect on overall efficiency as shown in Table 7. This table illustrates the results of treating a 1:3 dilution of pink water with 0.1% H_2O_2 through one to four units in series mode.

It would be difficult to determine the overall effect of units in series with just four units operating in a continuous flow mode with the small volumes used. Hypothetically, as the color of the solution disappears, the efficiency of the system is dramatically increased with direct passage of the colorless solution through units in series. The loss of energy by color absorption would be non-existent after the point of decolorization, thus increasing overall efficiency. This can be indirectly shown by diluting the pink water and examining TOC reduction per unit time. Studies were undertaken to examine this phenomenon using 1:1, 1:3, and 1:7 dilutions of pink water. Table 8 illustrates the results of these studies. There is a dramatic decrease of 91% in the TOC level of the pink after 3 hours of exposure in the UV-2000 system when the pink water is diluted 1:7 and only a 38% decrease with a 1:1 dilution. The relationship between these dilutions and the percentage of decrease in TOC observed after the exposure period appears to be proportional (fig 4). These results confirm the hypothesis concerning a significant increase in efficiency of the system with a decrease in color.

Effect of Wavelengths

Each of two aliquots of undiluted pink water containing 0.1% H_2O_2 was exposed to one of two wavelengths of UV light, 254 or 375 nm, in static mode, to determine if the higher wavelength were as effective in the destruction of explosives and reduction in TOC of treated solutions as the lower wavelength. The film depth of each sample was 40 mm, and each was exposed for 30 minutes. After the 30 minutes of exposure at 254nm, the pink water had completely decolorized and TOC had decreased from 89 mg/L to 9 mg/L. On the other hand, the color of the solution exposed at 375 nm was unexpectedly intensified, and no loss of TOC was noted. However, the TNT level in the pink water dropped to 0.02 mg/L after exposure at 375 nm and only to 0.15 mg/L after exposure at 254 nm. This failure to reduce the TOC level indicates that, although the higher wavelength uv-light will alter the TNT molecule, it apparently

Table 7. Evaluation of UV-2000 system operating in series mode

Parameters		Explosives content (mg/L)					
UV units (no.)	UV exposure (hr)	TNT	RDX	HMX	TNB	TOC	PNA
1	5	< 0.01	< 0.01	< 0.01	3.0	14.5	TNB
2	5	< 0.01	< 0.01	< 0.01	2.5	4.4	TNB
3	5	< 0.01	< 0.01	< 0.02	2.9	5.0	TNB
4	5	< 0.01	< 0.05	< 0.05	2.0	2.5	TNB

Note: A 1:4 pink water solution treated with 0.1% H_2O_2 was used as a sample.

Table 8. Alternatives for treatment of pink water

Parameters for 19 m^3pd pilot operation				Orig/Fin Analytical results (mg/L)[a]					
UV hrs/ Dilution	Total Volumes Treated m^3pd (gpd)	Operation based on flow rate (hr/day)	Oxidizing agent %	TNT	RDX	HMX	TNB	TOC	TLC[b]
1:4/3	(20,000) 75.7 m^3pd	20	0.3 oxone	28/0.01	26/0.01	27/0.02	trace/0	22.8/0.3	TNT/0 +PNA
1:2/3	(10,000) 37.9 m^3pd	10	0.3 oxone	64/0.01	55/0.01	8.5/0.02	trace/ 0.4	46.1/3/4	TNT/0 +2PA
1:4/3	(20,000) 75.7 m^3pd	20	0.2 oxone	23/0.01	19/0.01	2.4/0.02	trace/0	21.8/0.4	TNT/0 +2PA
1:4/3	(20,000)	20	0.1 + oxone 0.1 H_2O_2	23/0.01	20/0.01	2.5/0.02	trace/ 0.1	25.0/0.9	TNT/0 +2PA
1:4/5	(20,000)	20	0.1 H_2O_2	30/0.01	26.8/0.0	13.0/0.02	0/ 2.08	23/1.6	TNT/TNB +2PA
1:2/5	(10,000) 37.9 m^3pd	10	0.1 H_2O_2	64/0.01	48.0/0.0	56.9/0.05	0/ 0.9 2.5	45.4/13	TNT/TNB +2PA/+2PA

[a] TNT, RDX, and HMX were analyzed by LC; TNB was analyzed by GC.

[b] PA = Traces of polynitroaromatic compounds.

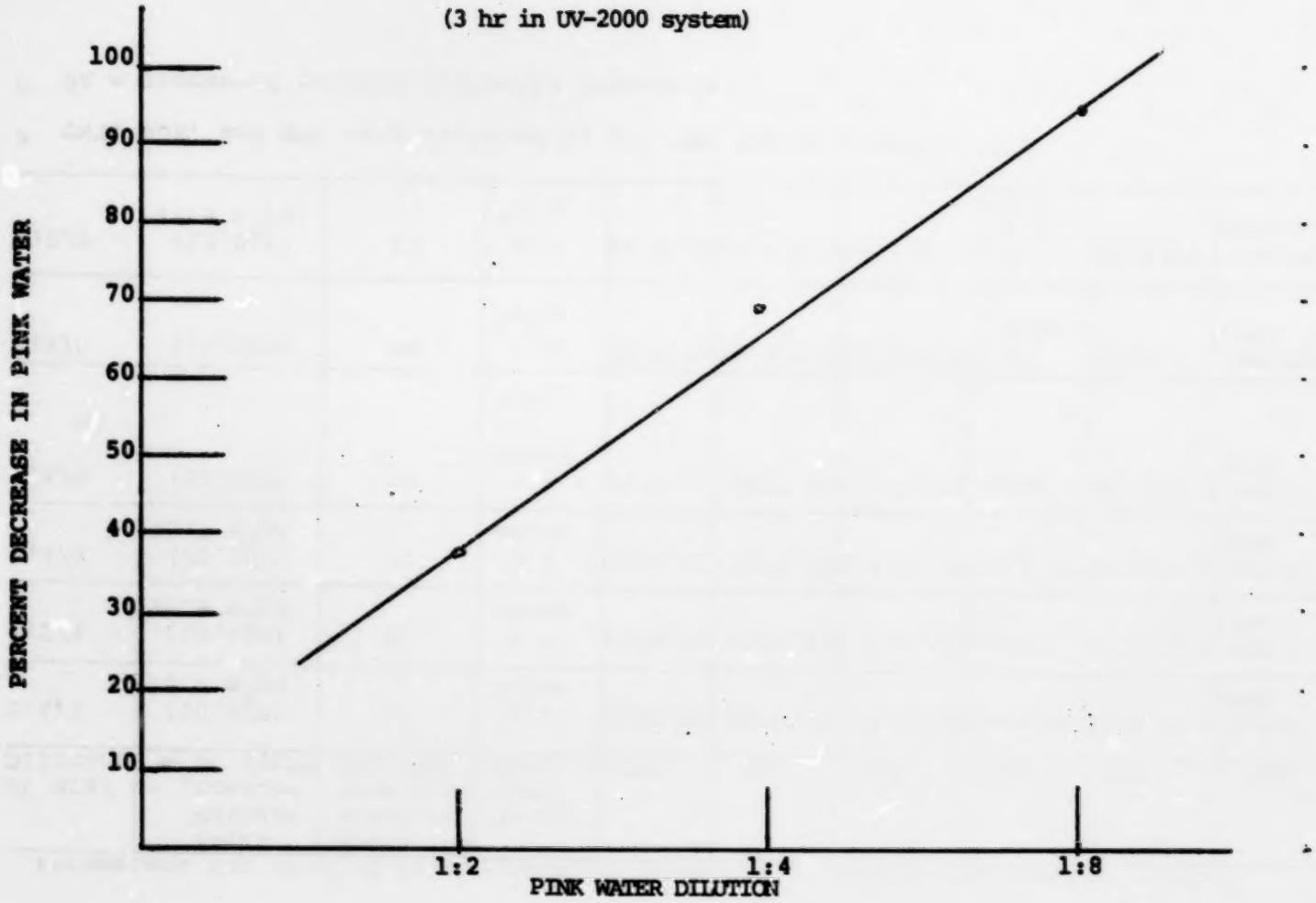

Figure 4. Effect of pink water dilution on TOC reduction

cannot oxidize it. The significant reduction of TOC and rapid decolorization observed with the sample irradiated at 254 nm is a good indication that this shorter wavelength has a pronounced effect on the overall efficiency and effectiveness of the photo-oxidation system.

Chemical Reactions

The proposed mechanism of action of the H_2O_2 and Oxone (monopersulfate compound) in the treatment is the production of OH radicals which are ultimately responsible for the destruction of the explosives in the water upon exposure to UV light. The mechanism of each is outlined below with RH representing the explosive.

$$H_2O_2 \rightarrow 2 \cdot OH$$

$$RH + \cdot OH \rightarrow R\cdot + H_2O$$

$$R\cdot \rightarrow \text{cleavage of ring}$$

$$HOOSO_3^- \rightarrow \cdot OH + \cdot OSO_3$$

$$RH + \cdot OH \rightarrow R\cdot + H_2O$$

$$R\cdot \rightarrow \text{cleavage of ring}$$

Additional Analyses

In addition to explosive analyses, the treated samples with the higher TOC levels (2 mg/L) were analyzed for nitrosoamines (ref 3,4) and sulfonates (ref 5,6). No detectable levels of these products could be found by TLC procedures (sensitivity 50 ppb) in samples irradiated in the UV-2000 or UV-500 system with either H_2O_2 or Oxone.

In each case using H_2O_2, the peroxide level was monitored in the treated samples. The levels of residual peroxide range between 30 and 100 ppm after 3 or 5 hours of exposure in the UV-2000 system and 1.5 hr in the UV-500 system. With direct passage (instead of recirculation) of the pink water through units in series, the H_2O_2 will probably be completely destroyed, since UV efficiency is enhanced with decolorization.

The pH of the pink water solutions containing H_2O_2

or Oxone was monitored before and after treatment. Before treatment, the pH values averaged 7.3 and 3.2, respectively. After treatment, the values fell to 6.4 and 2.4. If the extremely low pH of the treated water with oxone poses a problem, it can be economically and simply neutralized by the addition of lime after treatment and before discharge.

Design Parameters of Full-Scale Treatment System

If pink water is to be treated effectively in the system, it must be filtered to remove suspended solids before irradiation. This can be accomplished by use of a filter between the source of the effluent and the sump where it is discharged. The trapped explosive crystals could be reclaimed, if desired.

After eliminating the suspended solids, the liquid is diluted, if necessary, and pumped into a mixing tank where metered additions of hydrogen peroxide or Oxone are made. To be certain that a homogeneous solution is prepared, the pink water and oxidant are further mixed by an in-line triblender after which the mixture is pumped into the UV-system for treatment. Figure 5 illustrates the basic design of the system. After treatment, the water can be discharged directly into a sewer line or, if H_2O_2 were used as the oxidizer, it could be recycled through the system for diluting untreated pink water. The treated water originally containing Oxone cannot be recycled without further treatment, since residual amounts of potassium and sulfate ions in the treated water would increase with each fresh addition of oxone.

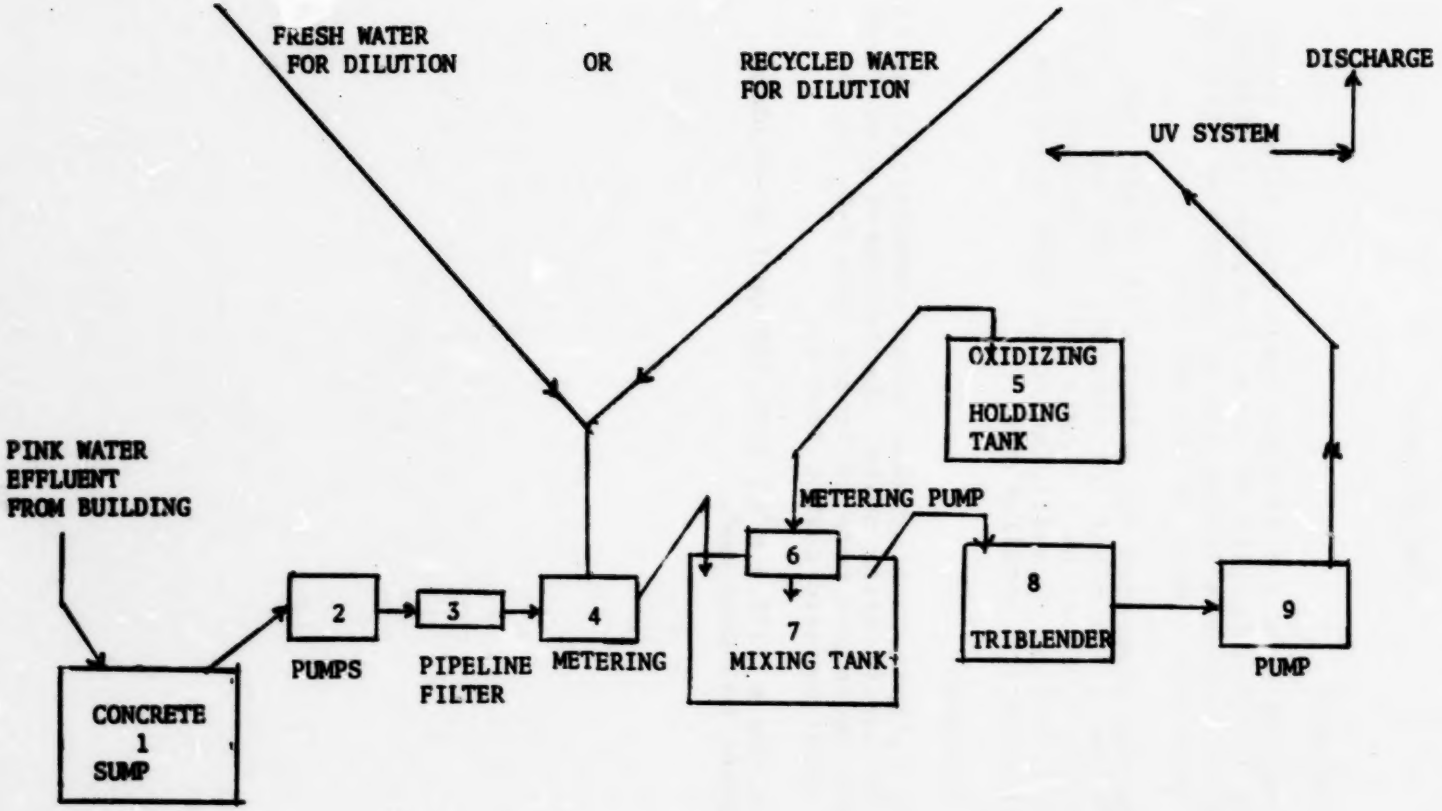

Figure 5. Basic design of the UV-oxidant system

CONCLUSIONS

UV-Ozone Treatment

1. Data obtained from a 3.79 m^3pd (1000 gpd) pilot plant demonstrated the feasibility of using uv-ozone to oxidize TNT and RDX in aqueous solution and to produce an effluent containing less than 1 mg/L of TNT and RDX.

2. A design was generated for a 18.9 m^3pd (5,000 gpd) modular uv-ozone pilot plant for treating pink water. The proposed design would allow a single unit to be used for low-flow applications or multiples to be used in-series for full mobilization requirements.

UV-Oxidant Treatment

1. From the optimization studies using commercially available UV water purification units, the treatment procedures incorporating Oxone are more efficient than H_2O_2 in reducing the total organic carbon levels.

2. A design for a 378.5 m^3pd (100,000 gpd) uv-oxidant treatment plant was proposed.

RECOMMENDATIONS

UV-Ozone Treatment

1. A 5000 gpd (18.9 m^3pd) pilot plant should be evaluated at an ammunition plant in order to determine the operating conditions required for achieving the minimum fixed and operating costs for a 378.5 m^3pd (100,000 gpd) plant.

2. An economic analysis should be performed on the 18.9 m^3pd (5000 gpd) unit after process parameters have been optimized.

UV-Oxidant Treatment

1. A study should be made to develop a new design for the UV-oxidant process that would be suitable for purification of larger volumes of pink water to enhance the economics of the process.

2. Further studies of the process should be made only if more cost-effective equipment is developed to process the volume and concentration of pink water to be expected in a full-scale plant.

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